# Fourier Transform Infrared Spectroscopy of Azide Ion in Reverse Micelles


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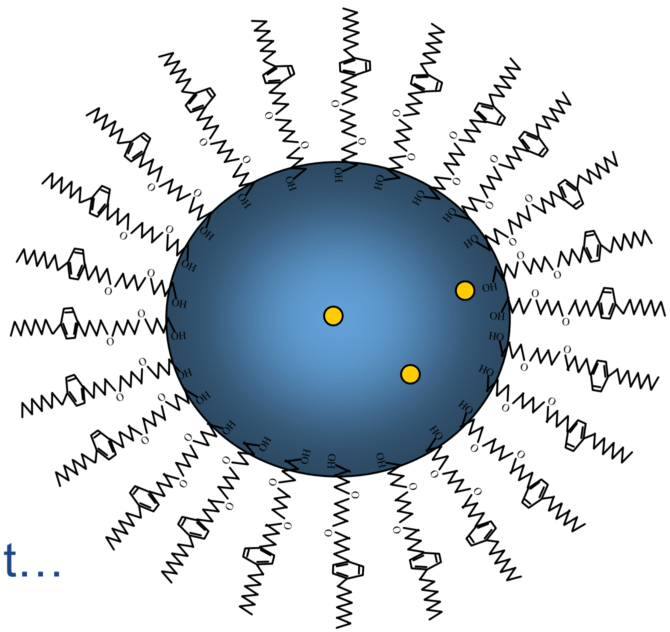
# Introduction

## 1. What are reverse micelles (RMs)?

Nanosize water droplets solubilized in oil phase by surfactants



## 2. Why studying RMs?

Wide range of applications —

Biocatalysis, drug delivery, nanoparticle fabrication, micro-reactor, solvation dynamics in confined environment…

## 3. How to study RMs?

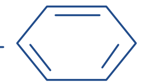
- Time-resolved fluorescence, dynamic light scattering – aggregation
- FTIR and Raman spectroscopy – structure
- Probe molecules (organic dye) – solvation interaction

## 4. Focus of this work:

- Sizes of NP RMs by Time-resolved fluorescence quenching
- FTIR of O-H stretch of water and C-O stretch of NP
- Vibrational band of azide ion to probe NP RMs

# Experimental

- **Materials**

  nonionic NPn $\rightarrow$ $C_9H_{19}-$  $-(OCH_2CH_2)_n-OH$ *(NP7/NP4=4)*

  anionic AOT $\rightarrow$ $(C_8H_{17}-O-\overset{\displaystyle O}{\overset{\|}{C}})_2CH-SO_3^-\ Na^+$

  cationic CTAB $\rightarrow$ $C_{16}H_{33}-N(CH_3)_3^+\ Br^-$

  $\omega = [H_2O]/[\text{surfactant}]$

- **FTIR** $\rightarrow$ Mattson 7020A (resolution: 1 $cm^{-1}$)

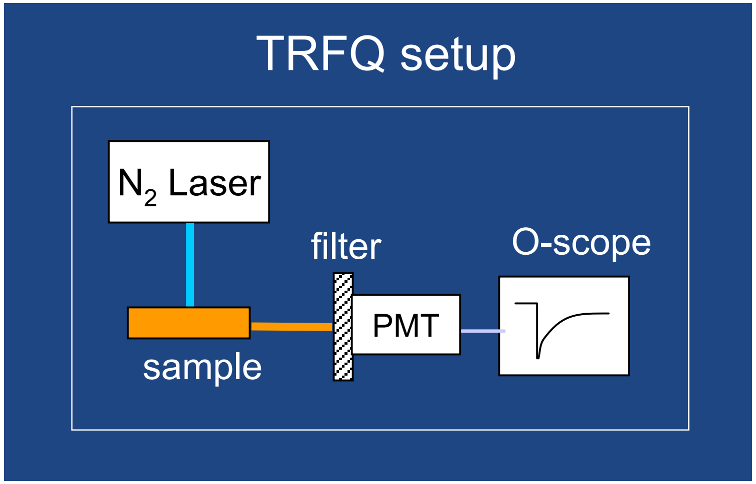
- **TRFQ**[a] $\rightarrow$ fluorophore dye: $Ru(bpy)_3(Cl)_2$
  quencher: methyl viologen

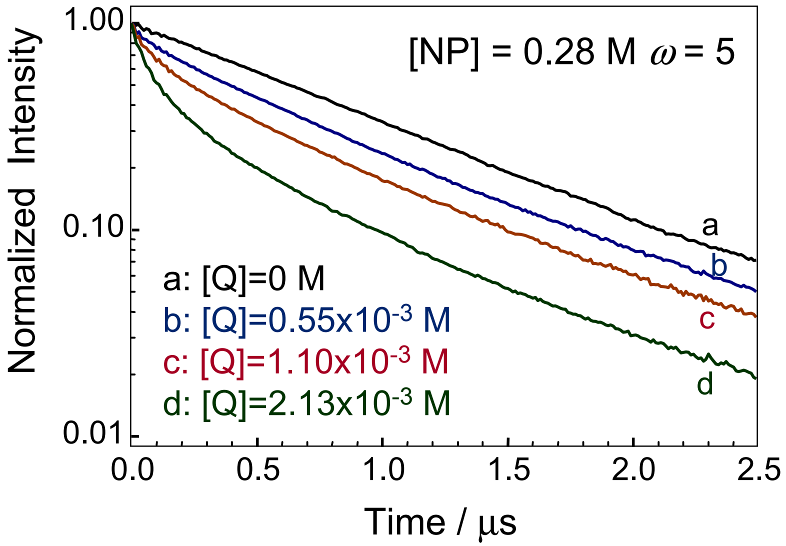
  [dye]/[M] < 0.04
  [Q]/[M]<1.2

[a] Lang *et. al. J. Phys. Chem*. **92**, 1946 (1988).

# Time-resolved fluorescence quenching

*Aggregation number + radius of NP RMs*




$$I(t) = I_0 \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\}$$

$$A_2 = k_0 + (k_e k_Q / A_4)[Q]$$

$$A_3 = [Q]/[M] \bullet (k_Q/A_4)^2$$

$$A_4 = k_Q + k_e[M]$$

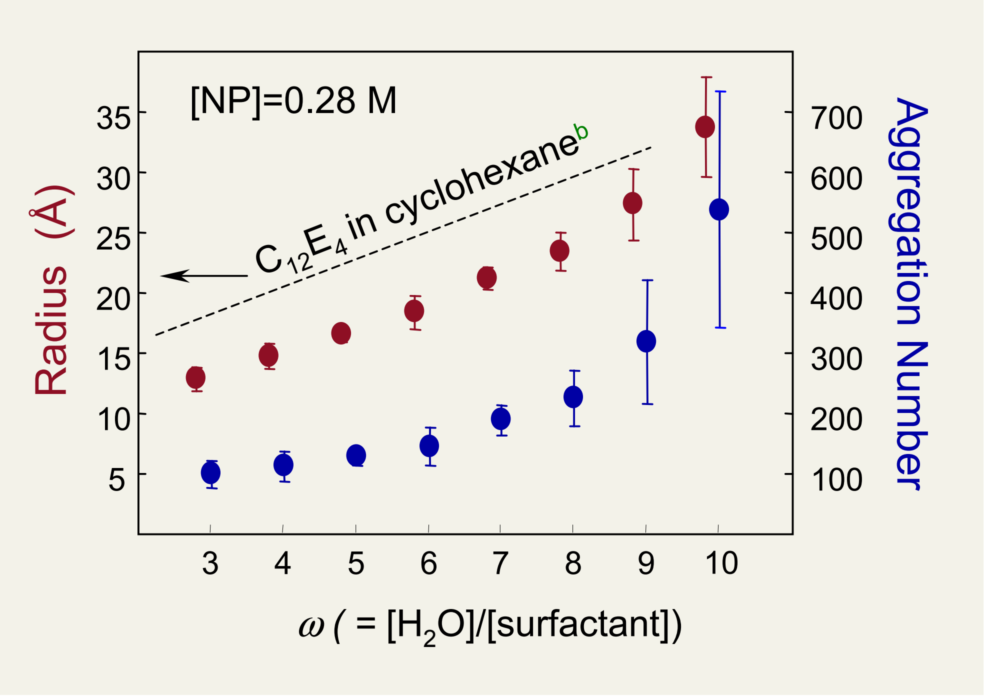
$$N = A_3([\text{surfactant}]-\text{CMC})/[Q] \bullet [(A_3A_4+A_2-k_0)/A_3A_4]^2$$

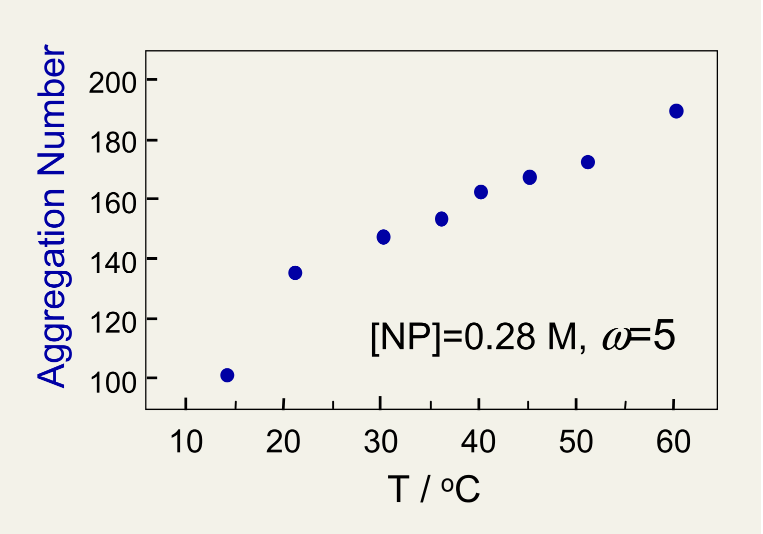
$$R_\omega = [3N\omega V_{H_2O} / 4\pi]^{1/3} \qquad \text{CMC} = 0.031\ \text{M} \qquad V_{H_2O} = 29.9\ \text{Å}^3$$

# Aggregation number of NP RMs in cyclohexane

NP RMs in cyclohexane:

- [NP] = 0.28 M, $\omega_{max}$ = 13
- $\omega_{max}$ increases with [NP]



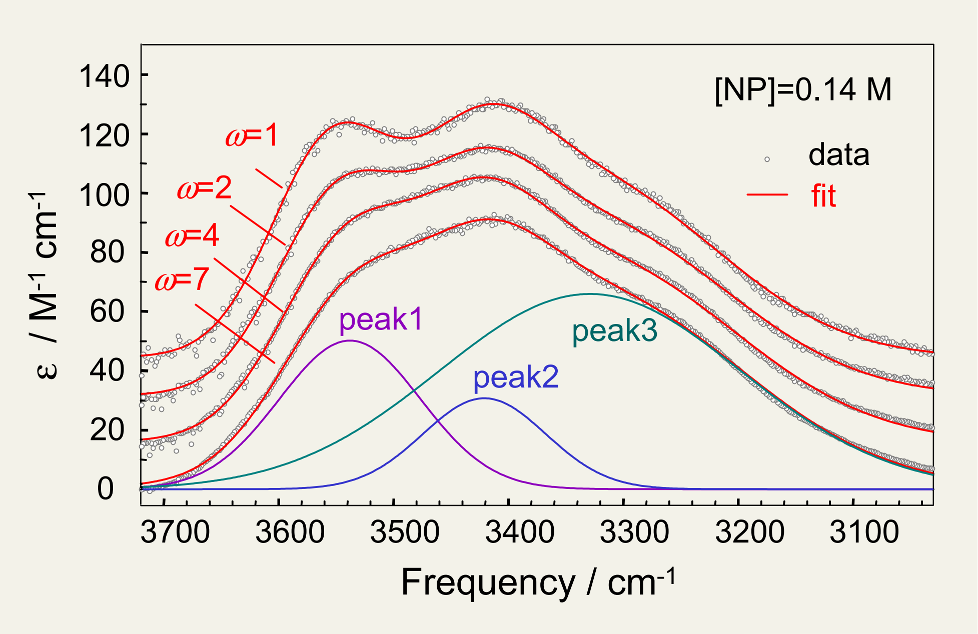



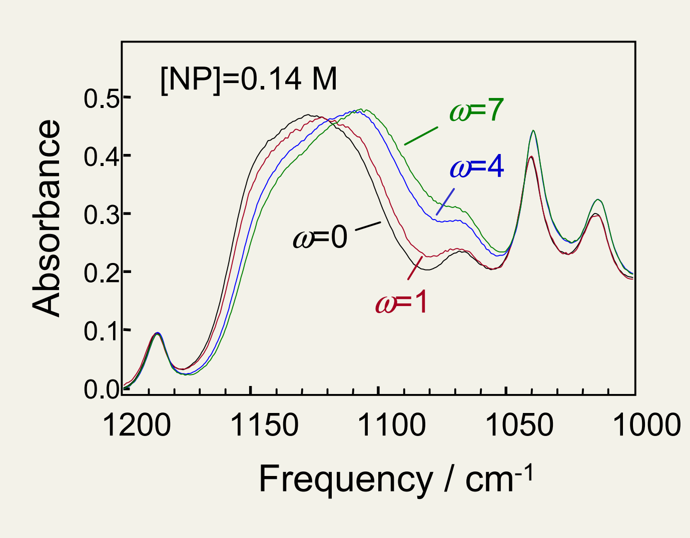

## Aggregation number :

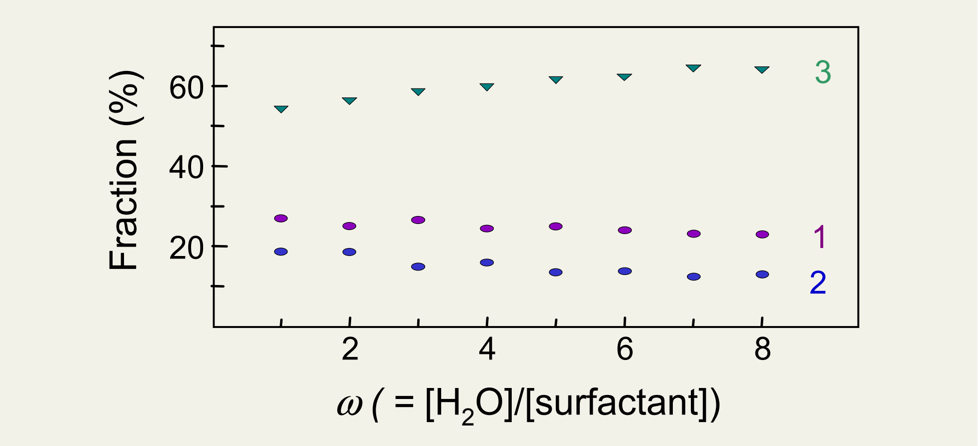
- increases with increasing $\omega$
- increases at elevated T
- independent of
  - concentration of NP
  - added sodium azide

[b] $C_{12}E_4$ in cyclohexane: Caldararu *et. al. Adv. Colloid and Interface Sci.* **89-90**, 169 (2001).

# FTIR of O-H and C-O stretch bands in NP RMs



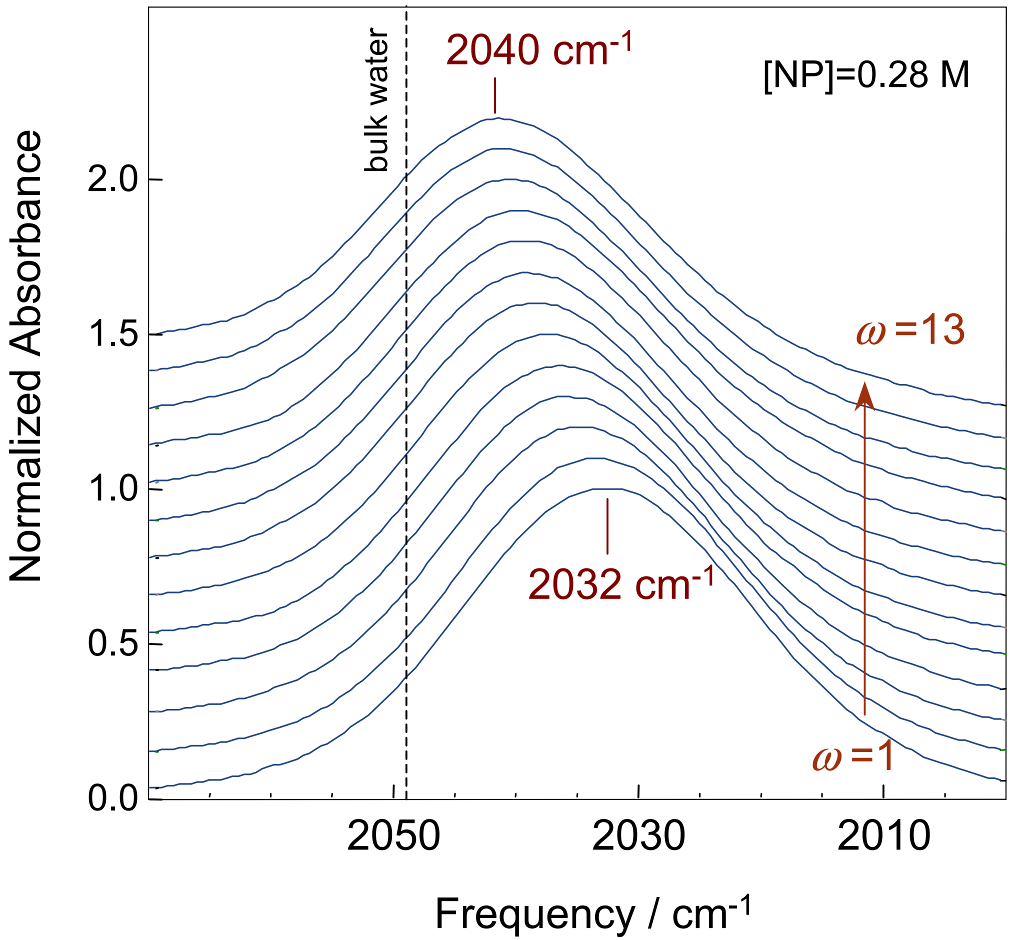




As $\omega$ increases:

- red-shift in C-O stretch
- water becomes more bulk-like

# Antisymmetric $\nu_3$ vibration of azide ion in NP RMs

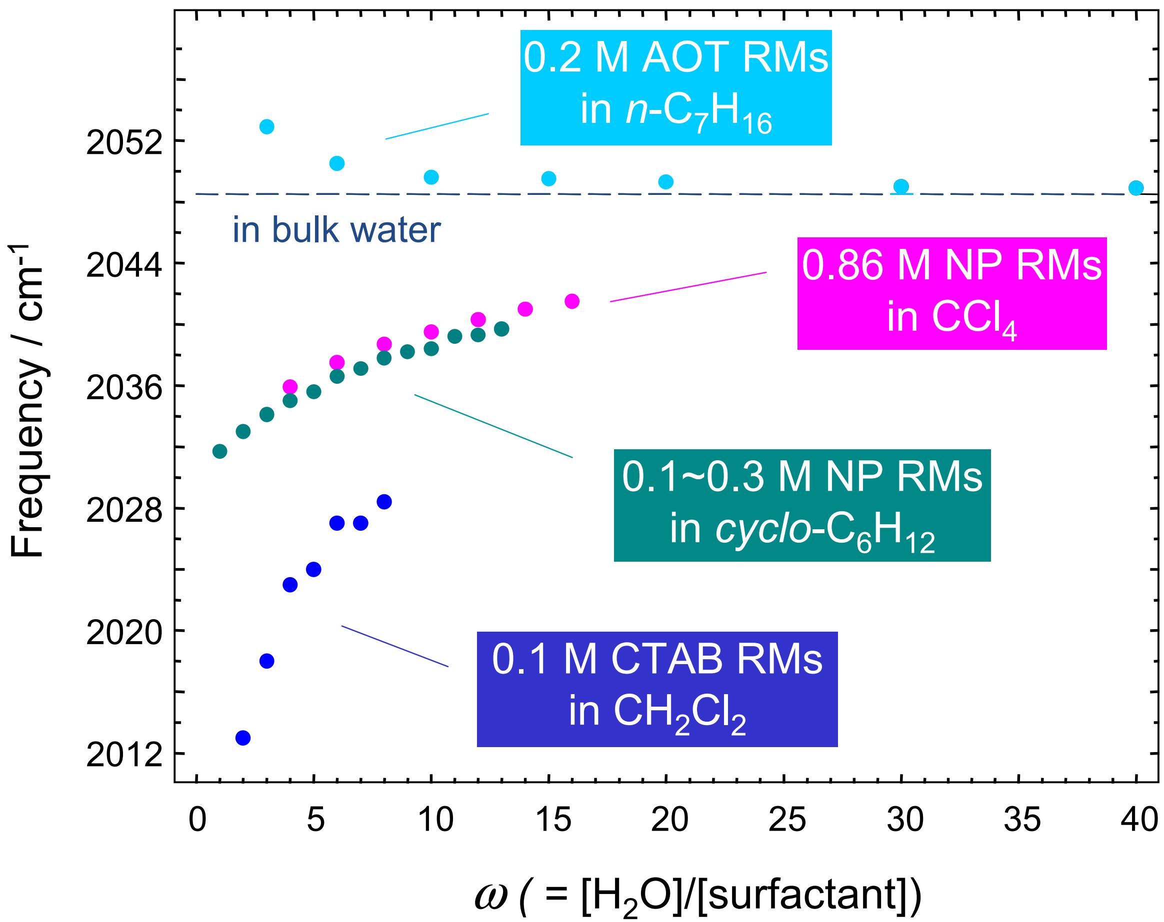



$^{\delta-}N = \overset{\delta+}{N} = N^{\delta-}$

## The $\nu_3$ band :

- in gas phase- 1987 $cm^{-1}$
- in bulk water- 2049 $cm^{-1}$
- shows no dependence on
  - *azide ion concentration*
  - *surfactant concentration*
  - *added salts*
- blue shift towards bulk at elevated T
- similar shift in C-N stretch of $OCN^-$ and $SCN^-$ ions

# Antisymmetric $\nu_3$ vibration of azide ion




## Possible causes for the $\nu_3$ shift :

- charge of the surfactant
- location of the ion
- polarity of water
- presence of $Na^+$

# Summary

- NP RMs grow in size with $\omega$
- Water become more bulk-like as $\omega$ increases
- $R_\omega$ = 13 ~ 34 Å for NP RMs at $\omega$ = 1 to 10

  $R_\omega$ is insensitive to [NP]
- The $\nu_3$ vibrational band of azide ion - *solute IR probe of RMs*
  - The $\nu_3$ frequency depends on the surfactant charge
    - blue shifts in AOT RMs compared to in bulk water
    - red shifts in NP and CTAB RMs compared to in bulk water
  - The $\nu_3$ band tends toward the bulk value with $\omega$
- Ongoing studies on RMs

  time-resolved dynamics – *vibrational relaxation*, *photodetachment, photodissociation, and recombination*

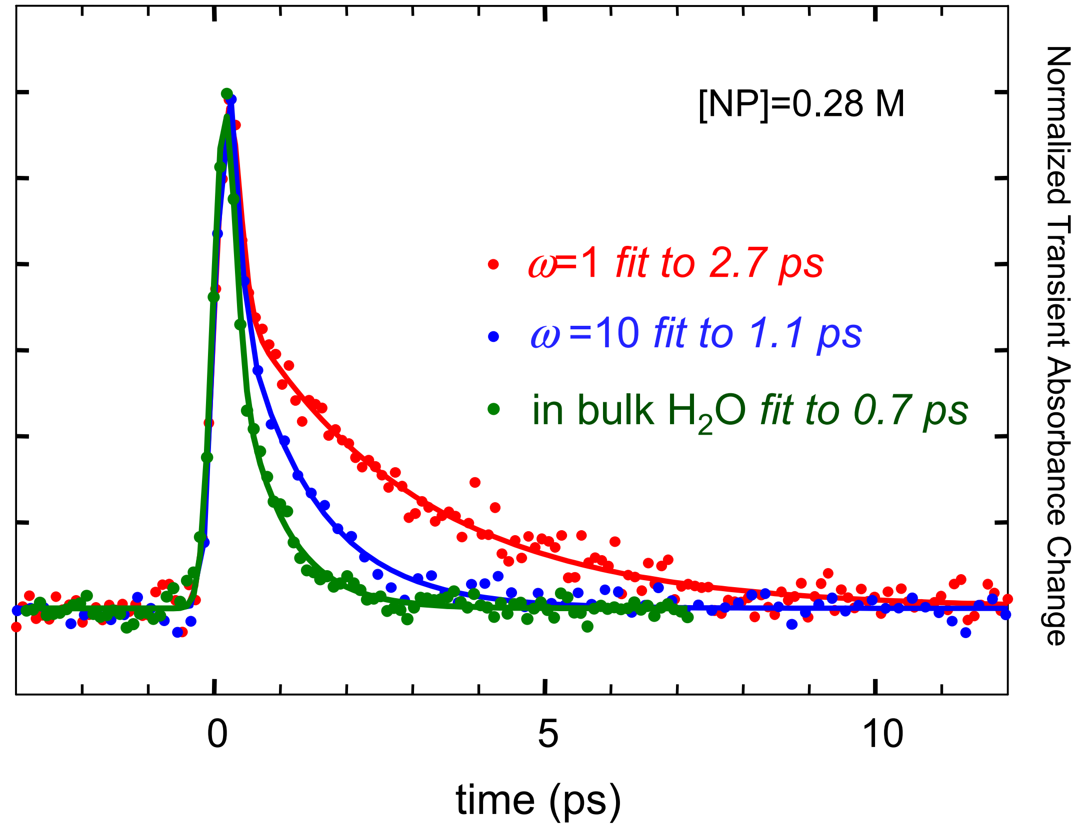
# Time-resolved dynamics in reverse micelle

- Relaxation rate depends on $\omega$ : shift towards the bulk value at large $\omega$
- Polarization dependent exp.

  vibrational relaxation
  reorientation time

- VIS pump – IR probe photodetachment, photodissociation, and recombination
- Surfactant charge effect on dynamics

**Vibrational relaxation of the $\nu_3$ band of azide in NP RMs by IR pump – IR probe**



# Acknowledgements

Jeff Owrutsky

Daniel Steinhurst

Andy Baronavski

Everett Carpenter

This work was supported by the office of Naval Research through the Naval Research Laboratory.

This work was performed while QZ held a Naval Research Laboratory – National Research Council Research Associateship.